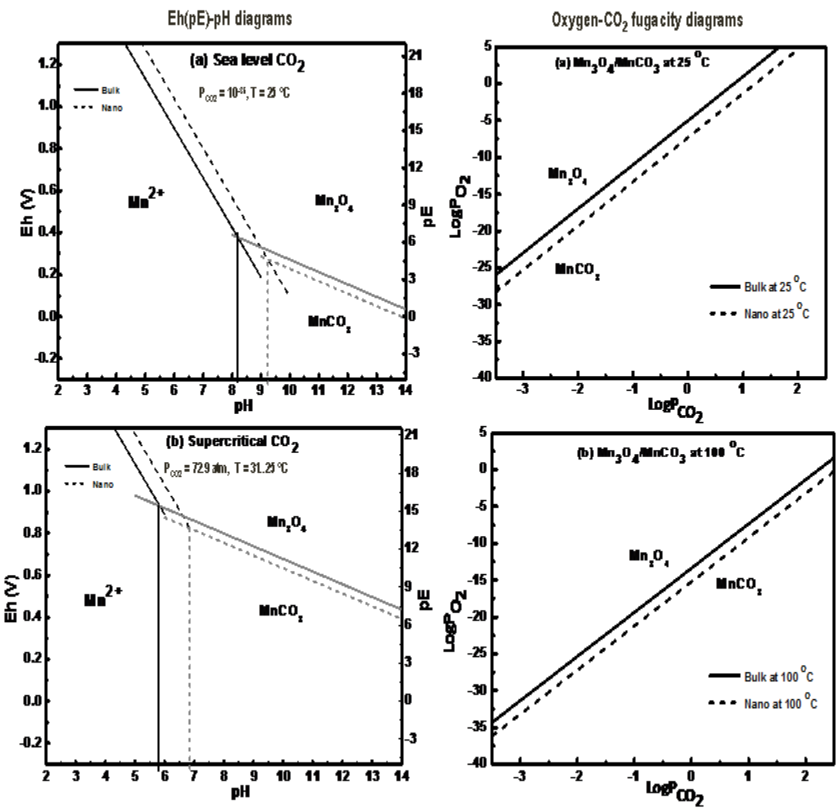
Manganese carbonate formation from amorphous and nanocrystalline precursors: Thermodynamics and geochemical relevance



Eh(pE)-pH and the oxygen-CO_2 fugacity diagrams for bulk and nanophase (10 nm) $Mn_2O_3/MnCO_3$ system

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Scientific Achievement

The particle size driven shifts were observed in oxidation potential (Eh, oxygen fugacity) and pH of $MnCO_3$–Mn_3O_4 phase boundaries calculated from calorimetrically measured surface energies. In supercritical CO_2, the expansion of the $MnCO_3$ stability field leads to significant reduction of the Mn_3O_4 stability field.

Significance and Impact

The Mn phases formation are controlled not only by redox potential but also by surface energy effects at the nanoscale with manganese oxides dominating at the nanoscale in aerated environment, while manganese carbonate is favored in coarse grained materials and reducing environments.

Research Details

We synthesized and measured the energetics of amorphous and nanophase manganese carbonates to understand their influence on crystal growth, surface reactivity and nanoscale properties of $MnCO_3$ using acid solution and water adsorption calorimetry.

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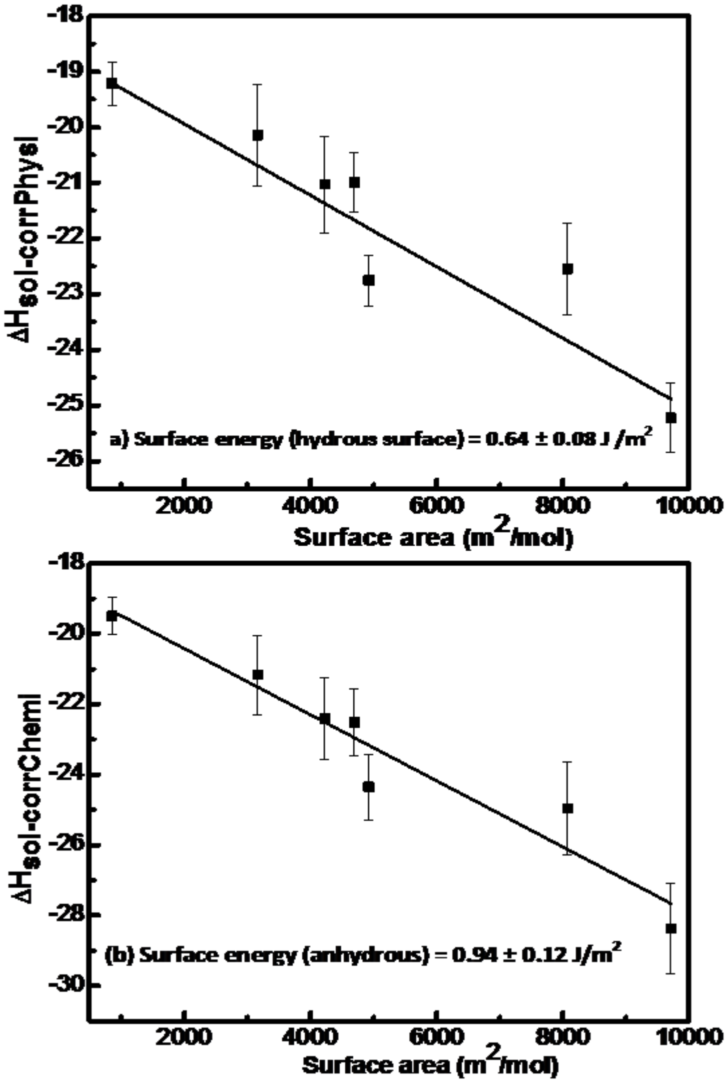

The solution enthalpies for nano $MnCO_3$ samples plotted against the surface area obtained by BET analysis. The solution enthalpies are corrected for contribution associated with surface water as physically ($\Delta H_{sol\text{-}corr\text{-}physi}$) and chemically ($\Delta H_{sol\text{-}corr\text{-}chemi}$) adsorbed water and they correspond to hydrous and anhydrous surfaces.

The surface enthalpy of $MnCO_3$ (0.9 ± 0.1 J/m^2) is lower than that of calcite (1.9 ± 0.2 J/m^2), which suggests the surface interactions of $MnCO_3$ are weaker than those of the calcite surface. Furthermore, the less exothermic water adsorption enthalpy of $MnCO_3$ (-66.6 ± 2.96 kJ/mol) compared to calcite (-96.26 ± 0.96 kJ/mol) supports weaker interaction on the MnCO3 surface.

The particle size driven surface energy effects could affect electrochemistry and catalytic properties of these materials and hence influence their geochemistry as well as various industrial applications.

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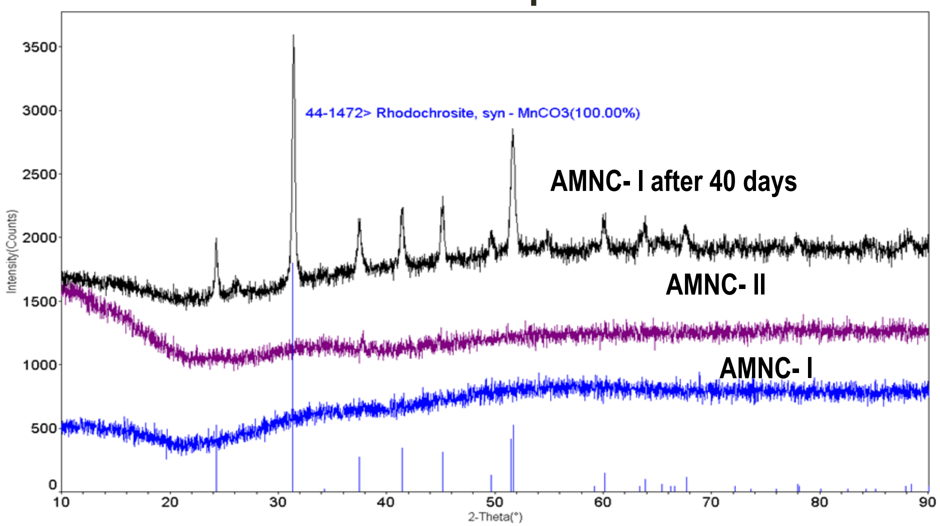
Powder XRD patterns



Amorphous $MCO_3.nH_2O$	Hydration (n) (mol) (TGA)	Enthalpy of Crystallization (ΔH_{crys}) (kJ/mol)	Ionic crystal radius M^{2+} (nm)
$MnCO_3.nH_2O$ (AMnC)	1.2 ± 0.04	-32.44± 0.71	0.083
$MnCO_3.nH_2O$ (AMnC)	1.78 ± 0.19	-31.62 ± 0.82	
$CaCO_3.nH_2O$ (ACC)	1.13 - 1.58	-17 ± 1 to -24 ± 1	0.1
$MgCO_3.nH_2O$ (AMC)	1.28	-35.8 ± 1.2	0.072
$FeCO_3.nH_2O$ (AFC)	1.75	-37.8 ± 9.8	0.078

- ➢ *Amorphous $MnCO_3$ (AmnC) is a metastable phase and it slowly crystallizes to rhodochrosite after 40 days*
- ➢ AMnC precursor provides a low energy pathway for $MnCO_3$ crystallization analogous to that observed in (Ca-Mg-Fe)CO_3 systems with crystallization enthalpies appear to be controlled by cation size.
- ➢ *Crystallization enthalpies of amorphous carbonates* become less exothermic with increase in ionic radius.

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